SYNTHESIS AND STUDY OF METHOXY-SUBSTITUTED DIENYNES

BY

WARREN LEWIS WALTON

B.S., Millsaps, 1935

M.S., Louisiana State University, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
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THE UNIVERSITY OF ILLINOIS, 1941

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Introduction

Methoxy substituted phenanthrenes have a close chemical relation to many vitally important organic substances. The sterols, compounds of the morphine series, and certain estrogenic substances have as part of their carbon skeletons the phenanthrene skeleton. One approach to such types is afforded by the ring closure which occurs when substituted dienynes are treated with acids. Di-$\triangle^{1,1'}$-cyclohexenyl-acetylene apparently undergoes ring closure to yield $\triangle^{13,14}$-dodecahydro-9-phenanthrone. Substitution designed to give hydrophenanthrones with one or more methoxyl groups at various points on the end rings would be valuable. An examination of the practicability of this synthetic method was therefore undertaken.

Discussion and Results

Substitution of methoxyl in the 3 position of di-$\triangle^{1,1'}$-cyclohexenylacetylene was abandoned when it was found that the direct approach namely, oxidation of resorcitol-monomethyl ether to 3-methoxy-1-cyclohexanone, failed due to the elimination of methyl alcohol.

The mono-methyl-ether of quinitol was readily converted to 4-methoxy-1-cyclohexanone. This ketone was condensed with acetylene in the presence of potassium *tert.*-amylate to yield 4-methoxy-1-ethynyl-1-cyclohexanol. Further condensation, through the Grignard complex of this acetylenic alcohol with cyclopentanone, 2-methyl-1-cyclopentanone, and 4-methoxy-cyclohexanone yielded three new acetylenic glycols. Two of these glycols were dehydrated yielding two new dienynes: 4-methoxy-$\triangle^{1}$-cyclohexenyl-$\triangle^{1}$-cyclopentenylacetylene and 4-methoxy-$\triangle^{1}$-cyclohexenyl-2-methyl-$\triangle^{1}$-cyclopentenylacetylene.

4-Methoxy-1-cyclohexanol-1-cyclohexanolacetylene was obtained by condensation of 4-methoxy-1-cyclohexanone with the Grignard complex of 1-ethynyl-1-cyclohexanol. The *cis* and *trans* forms of the glycol were separated by conversion to the *bis*-3,5-dinitrobenzoates followed by fractional crystallization and hydrolysis of the separated ester isomers. The mixed *cis* and *trans* glycols were treated with 40 per cent sulfuric acid to produce a mixture of the dienyne and a number of ketones. The presence of the ketones was demonstrated by reducing the dienyne and preparing 2,4-dinitrophenylhydrazones of the ketones. These derivatives were separated by chromatographic adsorption. The mixture consisted largely of three compounds; of these, two gave analyses corresponding to the derivative of the methoxyphenanthrone sought while the third proved to be the derivative of the ketone previously reported[1] as $\Delta^{13,14}$-dodecahydro-9-phenanthrone. More drastic treatment of the mixed ketones with sulfuric acid followed by reduction converted one of the methoxy ketones to the unsubstituted ketone mentioned above, leaving the other methoxy ketone unchanged. Dehydrogenation of the mixed ketones yielded phenanthrene, 3-methoxyphenanthrene, anthracene, and a fourth product which was probably 2-methoxyanthracene. These same ketones were shown to be the main products of the cyclization regardless of whether the dienyne, the *cis*-glycol, or the *trans*-glycol was used as the starting material.

Recently the question of formation of spirans has arisen.[2] In this study, no conclusive evidence on this point was obtained, however, the formation of anthracene by dehydrogenation may be taken as an indication that some spiran was present.

The method was shown to be of relatively little value as a synthetic route to methoxyphenanthrones since, under all conditions attempted, the product was a complex mixture.

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VITA

The writer was born Dec. 13, 1914 in Bunkie, Louisiana. His elementary and high school training was received in a number of schools in Louisiana. He attended by two year periods: Southeastern Louisiana College, Millsaps College, and Louisiana State University, receiving the B. S. in Arts and Science at Millsaps College in 1935 and the M. S. in Organic Chemistry at Louisiana State University in 1937. After working one year, he entered the University of Illinois in Sept. 1938. He has been employed as glass-blower at the U. S. Regional Soybean Laboratory during the last two years of his work for the degree of Doctor of Philosophy.

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